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PASSIVE-LITHIUM SECONDARY BATTERIES

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The deposition and discharge of lithium on an inert (nickel) substrate
was studied in propylene carbonate and methyl acetate. Cycling efficiencies
were higher in propylene carbonate, while the rate of corrosion of the
electrodeposit was lower. Adding SO_2, H_2O (< 1200 ppm) or nitromethane,

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20. Abstract (Cont.)

all possible "precursors," increased the cycling efficiencies in both solvents, and markedly decreased the corrosion rate in methyl acetate.

A mechanism of loss of cycling efficiency and long-term corrosion has been proposed, based upon the encapsulation of electro-deposited lithium by insulating lithium-solvent reaction products. Additives form Li^+-conductive films which retard encapsulation during plating, and, in the case of methyl acetate, during open circuit stand as well.

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PASSIVE-LITHIUM SECONDARY BATTERIES

The purpose of this program has been to explore the feasibility of a unique ambient temperature secondary battery system. This contains a passivated lithium anode and a soluble depolarizer. The lithium electrode is to be protected from attack by the solvent or cathode material by means of a "precursor" dissolved in the electrolyte which reacts with the metal to form a thin, protective layer. This protective film must allow lithium to discharge and replate. Passivation of the lithium allows the high charge and discharge rates characteristic of soluble depolarizers, such as $CuCl_2$.

This report deals exclusively with the rechargeable lithium electrode, which is the major problem area. Specific areas investigated have been the effect of electrolyte composition upon the lithium cycling efficiency, upon the cycle life, and upon the corrosion rate of the electrodeposited material. These variables were studied in three different electrolytic solvents: propylene carbonate (PC) (1), methyl acetate (MA) (2), and methyl pivalate (MP) (3). The electrolytes also contained 1M $LiClO_4$ or 1M $LiAlCl_4$ and, in some experiments, SO_2, nitromethane (NM) or H_2O. All of the latter additives were found to improve the behavior of the lithium electrode, and were considered as potential "precursors."

Results were first obtained for PC (1), as this is a most popular medium for lithium batteries. Deposition and discharge of lithium, usually 1 coul/cm^2, on an inert (nickel) substrate, were studied as a function of plating and stripping currents, cycle number and electrolyte composition. The cycling efficiency was usually less than 50% in the dry electrolyte (< 10 ppm H_2O, 1M $LiClO_4$), with higher efficiencies obtained at plating currents at 20-30 mA/cm^2. Water (< 1200 ppm), NM and SO_2 were all found to enhance the cycling efficiency. In all cases, marked deterioration of efficiency was noted after 10 to 20 repeated cycles. In the latter instance, visual inspection of the electrodes revealed slushy residues of lithium which could easily be wiped from the substrate, but which were not removable electrochemically. The electrodeposited lithium was found to corrode at an initial rate of 25-40 μA/cm^2, this rate decreasing somewhat with time. Within experimental error, the corrosion rate was independent of additive, although chronopotentiograms revealed the buildup of resistive films on the electrode during corrosion in the presence of such additives.

Next, the properties of the lithium electrode in MA/1M $LiClO_4$ were investigated (2). The efficiency of cycling lithium on nickel in such solutions containing less than 10 ppm H_2O was less than 10%.

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Addition of NM, SO_2 or small amounts of H_2O improved the efficiency markedly. Compared to PC, MA plus SO_2 or NM afforded more repeated cycles before failure of the working electrode. Unlike PC, the open circuit corrosion rate of electrodeposited lithium in MA is decreased in the presence of additives, e.g., from about 300 $\mu A/cm^2$ to 70 $\mu A/cm^2$ with >10^4 ppm NM, or to 0 $\mu A/cm^2$, under the proper conditions, with 3M SO_2.

Based upon the results in PC and in MA, a mechanism of loss of efficiency during cycling, as well as during open circuit stand following plating, has been formulated. Selim and Bro (4) have shown that the chemical reaction rate of electrodeposited lithium is about ten times less than the corrosion rate measured electrochemically, based upon strippable lithium. Thus a major pathway limiting the efficiency of lithium cycling seems to be the encapsulation of the electrodeposited metal by small amounts of solvent or impurity reduction products formed during plating onto the substrate. Similar reactions probably account for the corrosion of the high surface area deposits on open circuit stand. Water (< 1200 ppm), NM and SO_2 all increase significantly the efficiency of cycling lithium in both PC and MA, while only in MA do they decrease the lithium corrosion rate. The additives are postulated to form Li^+-conductive films on the granules of lithium as they are being formed. This allows the growth of larger grains than in the "pure" electrolyte, where their growth is limited by the formation of non-conductive films through reaction with the solvent. In addition, additives can adsorb onto the surface of the substrate, and limit the formation of insulating substrate areas (e.g., from solvent reduction), which effectively cut down the total plating area and lead to the formation of more easily encapsulated, dendritic deposits.

On open circuit stand, the conductive films are gradually replaced by insulating films. The competition between conductive and insulating film formation will depend, in part, upon the relative local solubilities of the two. In PC, the equilibrium appears to fall toward insulating film formation, while in MA, conductive film formation is more favorable. Hence, in MA we observe a true total passivation of the lithium deposit by the additives, as required in the proposed battery.

Clearly, one of the most problematic areas with the lithium electrode is the granular nature of the electrodeposited metal, which renders it susceptible to corrosion. Reaction between PC and lithium ribbon ("bulk" lithium) is not noticeable, even at high temperatures, due to the homogeneous nature of solvent-induced film. Analogously, precursors are likely to be more effective at passivating bulk lithium than electrodeposited lithium.
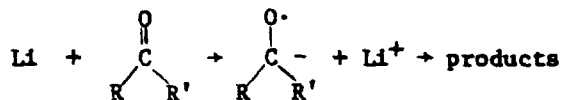
These films can be used to prevent attack of lithium by dissolved depolarizers. For example, lithium ribbon was exposed to solutions of PC saturated with $CuCl_2$, one of which contained 1M SO_2. Without SO_2,

the solution became colorless within a few hours, followed by a slow darkening of the lithium surface. With SO_2, the solution remained yellow for 4 to 5 days, then became colorless. The lithium remained shiny throughout. The SO_2-induced passivating film evidently slowed the reduction of Cu^{+2} to Cu^{+1} (colorless) and completely prevented the reduction of Cu°. We estimate from these data that the attack rate of Cu^{+2} on lithium decreased from >100 $\mu A/cm^2$ to ~5 $\mu A/cm^2$. The same experiment carried out for Fe^{+3} also showed slower reduction of the ion by lithium, although the lithium surface did evidently blacken in the presence of SO_2.

Within this model, then, the problems of low cycling efficiency and of corrosion of the electrodeposit are closely related. One approach to solving these problems is to search for an electrolyte which is truly unreactive toward lithium. For example, a possible mechanism for the reaction of lithium with MA involves the initial abstraction of the (relatively) acidic α hydrogen (3). To test this mechanism, the lithium cycling efficiency and corrosion rate was measured in methyl pivalate (I), in which such a reaction is impossible:

$$H_3C - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} - \overset{\overset{O}{\parallel}}{C} - OCH_3$$

(I)
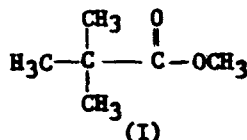
The study showed no advantage in using (I) instead of MA, with regard to cycling efficiency, corrosion rate, or the effect of additives. An alternative mechanism, which would apply to both linear and cyclic esters, and, with obvious modification to any molecule with a center of positive charge, is the reduction, through initial electron transfer, of carbonyls by lithium (5):

$$Li + \underset{R \quad R'}{\overset{O}{\overset{\parallel}{C}}} \rightarrow \underset{R \quad R'}{\overset{O\cdot}{\overset{|}{C}}} - + Li^+ \rightarrow products$$

Any such solvent having a dielectric constant high enough to dissolve lithium salts is likely to undergo a similar reaction, so that the possibility of some reaction between lithium and solvent may be extremely difficult to eliminate, although its kinetics may be favorably slow.

It can be concluded from this work that an electrolyte for use in secondary lithium batteries, if not totally unreactive toward

lithium, should be capable of forming an Li^+-conductive film on the as-deposited metal, either through reaction with the solvent or with an additive (precursor). For use with a soluble depolarizer, the ideal electrolyte would contain an inert solvent and a precursor. Problems of morphology could be controlled in such electrolytes, as the presence of insulating reaction products would not limit the grain size of the deposited metal. Finally, an improved morphology indicates a deposit of lower surface area. Passivation of such deposits against attack by a soluble depolarizer, through use of a precursor, would be more easily achieved.

Of the solvent-precursor combination examined, MA/SO_2 is the most favorable. With the precursors studied, PC has been shown to be unsuitable for use as a solvent in secondary lithium batteries.

REFERENCES

1. R. D. Rauh and S. B. Brummer, Technical Report No. 1, Contract No. N00014-74-C-0205 (Feb. 1975).

2. R. D. Rauh and S. B. Brummer, Technical Report No. 2, Contract No. N00014-74-C-0205 (Feb. 1975).

3. R. D. Rauh, Technical Report No. 3, Contract No. N00014-74-C-0205 (Feb. 1975).

4. R. Selim and P. Bro, J. Electrochem. Soc., 121, 1457 (1974).

5. H. O. House, Modern Synthetic Reactions (New York: W. A. Benjamin, Inc., 1965), Ch. 3.